# REGENERABLE ADSORBENTS FOR THE ADSORPTIVE DESULFURIZATION OF TRANSPORTATION FUELS FOR FUEL CELL APPLICATIONS

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## Introduction

The requirement of ultra-clean transportation fuels, particularly, gasoline and diesel, has resulted in a continuing worldwide effort to dramatically reduce the sulfur levels in them. The presence of sulfur in these fuels is a very serious environmental concern because on combustion in the internal combustion engines, the sulfur is converted into toxic SOx. The Government agencies in various countries have implemented more stringent regulations for refineries to produce gasoline and diesel fuels with reduced sulfur content. For instance, the U.S EPA recently issued a new Tier II regulation that mandates refineries to reduce the sulfur content of gasoline from the current average of 300 ppmw to 30 ppmw by 2005-2006 and to cut down the sulfur content of highway diesel fuel from the current limit of 500 ppmw to 15 ppmw by 2006. Lowering the sulfur content in transportation fuels not only reduces the SOx emission, but it also contributes to reducing the emissions of other noxious gases such as NOx and hydrocarbons by allowing the automotive catalytic converters to work better.

The need for the production of ultra-clean gasoline and diesel fuel is further motivated by the rapid development of fuel cells for mobile, stationary and portable power application for which the sulfur levels need to be further reduced down to 1 ppmw. Hydrodesulfurization (HDS) using sulfided Ni-Mo or Co-Mo catalyst at high temperature and high pressure is a conventional method being employed by the refineries to produce low sulfur gasoline and diesel in order to meet the environmental regulations.[1,2] However, the process is inefficient to produce ultra-clean transportation fuels, particularly for fuel cell applications. Alternative methods such as adsorptive desulfurization, oxidative and extractive desulfurization, biodesulfurization, etc. are being developed in recent years to produce ultra-low-sulfur gasoline and diesel fuels.

Among the alternative methods, adsorptive desulfurization is a promising approach and several new processes, such as IRVAD and Philips S-Zorb processes have been reported recently.[3,4] The challenges in the adsorptive desulfurization include the following: (i) the adsorbent should be selective to remove only sulfur compounds without adsorbing the aromatics and olefins present the fuel; (ii) for on-board or on-site fuel cell applications, the adsorptive desulfurization should be performed at close to the ambient temperature; and (iii) the adsorbent should be regenerable for subsequent use.

A new process concept is being developed in our laboratory at PSU known as selective adsorption for removing sulfur (PSU-SARS) for the adsorptive desulfurization of gasoline, diesel and jet fuel.[1,2,5,6] Here we report what may be characterized as the "sense and grab" and "sense and shoot" approaches employed for selectively removing organic sulfur compounds present in these fuels. In the former approach, the sulfur compounds are selectively adsorbed onto certain adsorbents. The adsorbed sulfur compounds are recovered and the adsorbents are regenerated either by solvent washing or by oxidative regeneration. In the "sense and shoot approach", the sulfur compounds adsorbed onto the adsorbents are decomposed because of the occurrence of surface reactions with adsorbents. The sulfur is retained on the surface of the adsorbent and the remaining organic moiety is added to the fuel. The performance of the adsorbents is regained by reductive regeneration or a combined oxidative and reductive regeneration. In this communication we show few examples for our approaches for the desulfurization of diesel fuels and regeneration of adsorbents by solvent washing and reductive regeneration methods.

## Experimental

A wide variety of materials, including metal ions loaded on zeolites or mesoporous materials, mixed metal oxides, hydrotalcite-like anionic clays, metal modified activated carbon, supported metals, etc were tested as adsorbents. Most of these materials were synthesized in our laboratory as described elsewhere.[1,2,5,6] Either a model fuel containing thiophene (as representative for gasoline) or 4,6-Dimethyldibenzothiophene (4,6-DMDBT; as representative for diesel fuel) or commercial real gasoline / diesel fuels were used as a feedstock. The adsorbent was packed in a stainless steel column with an internal diameter of 4.6 mm and length of 150 mm. The adsorbent bed volume was 2.49 ml. Adsorbents such as zeolite-based, activated carbon and mixed oxides were initially activated at 200°C in $N_2$ flow to remove any adsorbed gases and then cooled down to the adsorption temperature (60°C). Sulfur-free n-decane was fed into the column using a HPLC pump at a rate of 0.2 ml/min. (LHSV = 4.8 h$^{-1}$) for about 10 min to remove entrapped gases and then switched to the sulfur containing feed with the same space velocity. Samples were collected periodically and their total sulfur contents were determined using an Antek 9000 Series Sulfur Analyzer (detection limit 0.5 ppmw). A GC equipped with a sulfur selective pulsed flame photometric detector (PFPD) was used to identify the nature of sulfur compounds present in the feed and effluent.

Regeneration of spent adsorbent was performed by solvent washing, oxidative or reductive regeneration. In the solvent washing method, a 1:1 mixture of methanol and toluene was flowed through the adsorbent bed at 70°C until the sulfur in the washing solvent became undetectable. The oxidative regeneration was effected by treating the spent adsorbent by flowing air at 300°C for 2-3 h while the reductive regeneration was performed by flushing the adsorbent with $H_2$ gas at 500°C for 2-3 h.

## Result and Discussion

The sulfur compounds present in gasoline, jet fuel and diesel are derivatives of thiophene (T), benzothiophene (BT) and dibenzothiophene (DBT), respectively. The reactivity of these sulfur compounds in the HDS reaction decreases in the order; thiophene (100) > benzothiophene (30) ≥ dibenzothiophene (30) > MDBT (5) > DMDBT (1).[7,8] The GC chromatograms obtained using a sulfur selective PFPD for two kinds of low sulfur diesel received from commercial sources are shown in Fig. 1. As can be seen, the 4,6-DMDBT is present as a major sulfur compound even in the diesel fuel containing below 10 ppmw of sulfur. This is the most refractory sulfur compound and is very difficult to remove by the existing the HDS process because of the steric hindrance exerted by the presence of methyl groups at the 4 and 6 positions.

In order to develop regenerable adsorbents for the desulfurization of diesel fuels, a wide variety of new adsorbents based on zeolites, mixed metal oxides, activated carbon and supported metal compounds have been tested using a model diesel fuel containing 220 ppmw of sulfur as 4,6-DMDBT in a

mixture of decane and hexadecane solvents. The breakthrough curves for the adsorptive removal of 4,6-DMDBT from the model diesel fuel at 60°C over transition metal oxides supported on MCM-41 mesoporous material and activated carbon are shown in Fig. 2. It is interesting to note that in both cases, the 4,6-DMDBT has been completely removed. The MCM-41-based adsorbent exhibits a breakthrough capacity of 3.5 mg of sulfur per g of adsorbent while the transition metal supported on activated carbon shows very high breakthrough capacity of 12.6 mg/g of adsorbent.
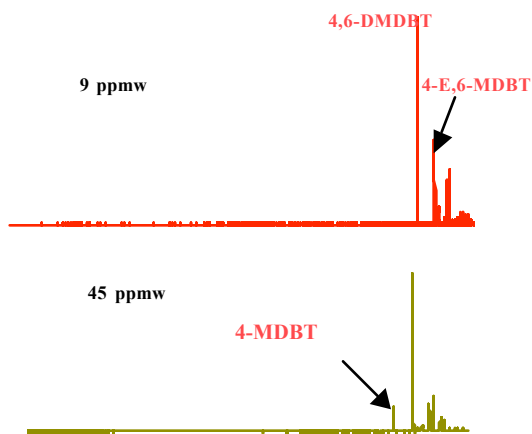


**Fig. 1.** Sulfur selective GC PFPD Chromatogram of low sulfur diesel fuels containing 9 ppmw and 45 ppmw sulfur
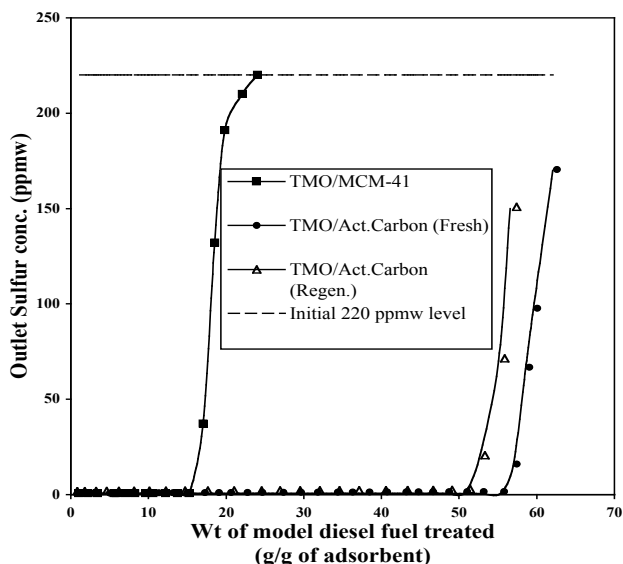


**Fig. 2.** Breakthrough curves for the adsorptive desulfurization of a model diesel fuel containing 4,6-DMDBT at 60°C over Transition metal oxides supported on MCM-41 and activated carbon. LHSV = 4.8 h$^{-1}$

      Attempt has been made to regenerate these adsorbents by flushing with a 1:1 mixture of methanol and toluene at 70°C. In order to estimate the amount of solvent required to completely recover the 4,6-DMDBT and to regenerate the adsorbent for subsequent use, the fractions of the solvent have been collected and analyzed using the total sulfur analyzer. The profile for recovering the 4,6-DMDBT by solvent washing from the spent

activated carbon-based adsorbent is shown in Fig.3. The sulfur content in the initial few fractions exceeded 1000 ppmw and then decreases exponentially. The results indicate that most of the sulfur compounds could be recovered using 20 cc of the solvent per g of adsorbent. However, about 100 cc of the solvent is required under the present experimental condition for the complete removal of all the sulfur compounds adsorbed on this particular adsorbent.
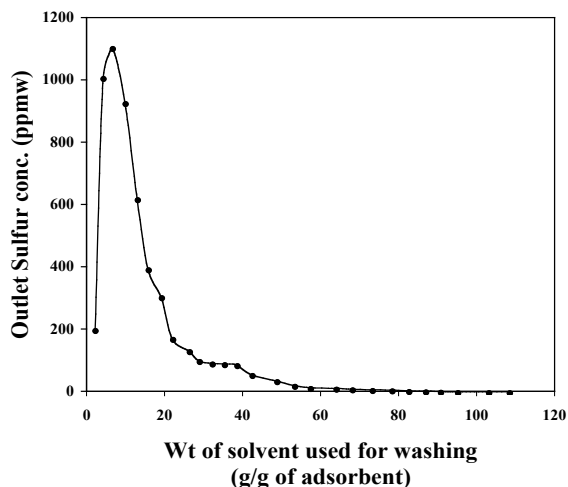


**Fig.3.** Profile for recovering the adsorbed 4,6-DMDBT by solvent washing from the spent activated carbon-based adsorbent at 70°C

      After the solvent washing, the regenerated adsorbent has been flushed with N$_2$ gas (40 ml/min) for about 1 h at 300°C in order to remove any adsorbed solvent molecules. Desulfurization of model diesel fuel over regenerated adsorbent has been performed under the same experimental condition as that of fresh sample and the sulfur breakthrough curve obtained on the regenerated sample is shown in Fig. 2 itself along with that of fresh samples. The breakthrough curves of fresh and regenerated samples are close to coincidence and this indicates that solvent washing can regenerate the adsorbent almost completely. This observation infers that the adsorbent simply grabs the sulfur sulfur compound (4,6-DMDBT) from the fuel and holds it by some weak interactions without destroying. Flushing with solvent is sufficient to break such weak interactions.

      There are several advantages of solvent washing for the regeneration of spent adsorbent. For instance, the organic sulfur compounds can be recovered by separating them from the solvent and the concentrated sulfur compounds can be treated in small HDS reactors to remove sulfur and the remaining organic moiety can be blended with the fuel.[1,2] Regeneration by solvent washing is an environmentally benign method because it avoids the emissions of SOx generated by oxidative regeneration or H$_2$S generated in the reductive regeneration.

      In the "sense and shoot" approach, model and real diesel fuels have been treated over adsorbents such as Ni supported on SiO$_2$-Al$_2$O$_3$, and nano-composite materials derived from hydrotalcite-like anionic clays. These materials exhibit better adsorption performance at relatively elevated temperature of around 200°C. This indicated that the sulfur compounds over these adsorbents are removed by surface reactions rather than weak interactions. Experiments using model fuels revealed that the sulfur compounds are destroyed and converted into

corresponding organic moiety although no hydrogen gas has been used during the adsorption.

Fig.4 shows the breakthrough curves for the adsorptive desulfurization of a low sulfur diesel fuel containing 45 ppmw of sulfur shown in Fig. 1. (bottom panel). In addition to the 4,6-DMDBT, the fuel contained 4-ethyl-6methyl dibenzothiophene (4-E,6-MDBT) which is even more refractory than the 4,6-DMDBT because of the presence of ethyl group instead of methyl group in the 4th position. The results indicate that the adsorbent is capable of sensing the sulfur compounds from this very dilute feed (feed containing only 45 ppmw of sulfur) and removing them completely (below 1 ppmw) by the surface reaction. The adsorbent has been regenerated by treating with $H_2$ gas at 500˚C for 1-2 h and then reused for the subsequent run. The breakthrough curves of the regenerated adsorbent in two cycles, also shown in Fig.4, indicate that the adsorption performance can be completely regained by the reductive regeneration.
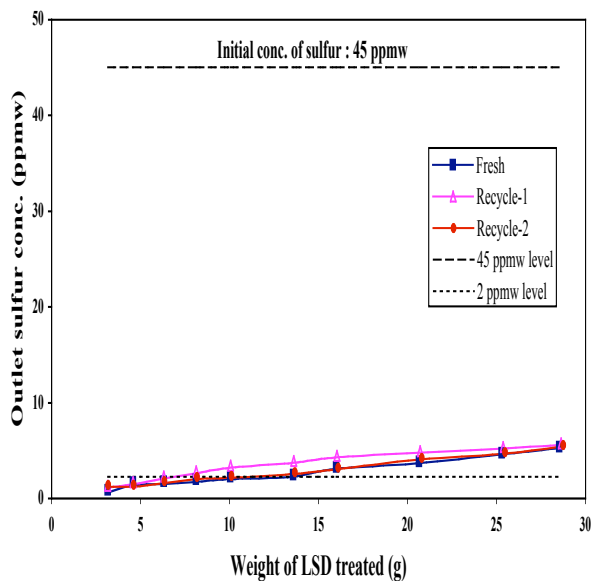


**Fig. 4.** Breakthrough curves for the adsorptive desulfurization of low sulfur diesel containing 45 ppmw of sulfur over a Ni-based adsorbent at 200˚C. LHSV = 4.8 h$^{-1}$

Several other adsorbents are currently being evaluated using the "sense and grab" and "sense and shoot" approaches in order to develop highly efficient and regenerable adsorbents for the production of ultra-clean gasoline, diesel and jet fuel for refinery and fuel cell applications and the detailed results will be reported.

## Conclusions

New regenerable adsorbents based on zeolites, mesoporous materials, activated carbon, supported metal, etc, are being developed for the selective removal of organic sulfur compounds present in gasoline, diesel and jet fuels using "sense and grab" and "sense and shoot" approaches. In the former approach, certain adsorbents such as metal oxide supported on activated carbon simply grabs the 4,6-DMDBT present in the model diesel fuel at 60˚C and hold it by some weak interactions without chemical reaction. The adsorbed sulfur compound could

be recovered by solvent washing and the adsorbent could be completely regenerated for subsequent use. On the other hand, in the sense and shoot approach, the adsorbent such as supported Ni metal, adsorbs the sulfur compounds at elevated temperature. The adsorbed sulfur compounds are decomposed and the remaining organic moiety is added to the fuel. The adsorbent could be regenerated by reductive regeneration at 500˚C using hydrogen gas.

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